# Horizontal and vertical food web structure drives trace element trophic transfer in Terra Nova Bay, Antarctica[☆]

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## ABSTRACT

Despite a vast amount of literature has focused on trace element (TE) contamination in Antarctica during the last decades, the assessment of the main pathways driving TE transfer to the biota is still an overlooked issue. This limits the ability to predict how variations in sea-ice dynamics and productivity due to climate change will affect TE allocation in the food web. Here, food web structure of Tethys Bay (Terra Nova Bay, Ross Sea, Antarctica) was first characterised by analysing carbon and nitrogen stable isotopes ($\delta^{13}$C, $\delta^{15}$N) in organic matter sources (sediment and planktonic, benthic and sympagic primary producers) and consumers (zooplankton, benthic invertebrates, fish and birds). Diet and trophic position were also characterised using Bayesian mixing models. Then, relationships between stable isotopes, diet and TEs (Cd, Cr, Co, Cu, Hg, Ni, Pb and V) were assessed in order to evaluate if and how horizontal (organic matter pathways) and vertical (trophic position) food web features influence TE transfer to the biota. Regressions between log[TE] and $\delta^{13}$C revealed that the sympagic pathway drives accumulation of V in primary consumers and Cd and Hg in secondary consumers, and that a coupled benthic/pelagic pathway drives Pb transfer to all consumers. Regressions between log[TE] and $\delta^{15}$N showed that only Hg biomagnifies across trophic levels, while all the others TEs showed a biodilution pattern, consistent with patterns observed in temperate food webs. Although the Cd behavior needs further investigations, the present findings provide new insights about the role of basal sources in the transfer of TEs in polar systems. This is especially important nowadays in light of the forecasted trophic changes potentially resulting from climate change-induced modification of sea-ice dynamics.

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## 1. Introduction

Despite Antarctica is a remote area, commonly seen as a pristine environment, many scientific researches carried out in the last decades revealed that contamination is a relevant issue, due to combined natural and anthropogenic sources. In Antarctic coastal areas, seasonal dynamics of sea-ice melting and phytoplankton production are the main factors controlling trace element (TE) concentration in seawater: as the sea-ice formation sequesters nutrients and TEs in winter, the following sea-ice melting, during the austral summer, releases them again in the surface water, fuelling pelagic production (Frache et al., 2001; Grotti et al., 2005; Illuminati et al., 2017). At the same time, pack-ice is a seasonal habitat for many microscopic organisms, called "sympagic" or "sea-ice" organisms, which represent additional sources of organic matter and TEs for pelagic consumers as soon as ice melts, and also for benthic organisms once settled on the seafloor (Grotti et al., 2005; Morata et al., 2011; Wing et al., 2018). High TE levels have been reported also in macroalgae (Runcie and Riddle, 2004), as well as in many pelagic and benthic consumers at different trophic levels (e.g. Cipro et al., 2017; Grotti et al., 2008; Negri et al., 2006; Trevizani et al., 2016), up to pelagic and benthic fish (Bustamante et al., 2003) and birds (Becker et al., 2016; Calle et al., 2015; Carravieri et al., 2013).

Despite the great effort made so far, the knowledge of TE transfer processes is still scanty. In particular, despite the

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acknowledged key ecological role of phytoplankton and sea-ice algae in the Southern Ocean (Petrou et al., 2016), as well as their tendency to bioaccumulate a wide range of TEs, little is known about their role as potential drivers of element transfer to upper trophic levels. Moreover, the majority of research on contaminant biomagnification focused on single elements (e.g. Hg: Bargagli et al., 1998; Cipro et al., 2017) or only a few taxa (Carravieri et al., 2013; Pereira Majer et al., 2014). In turn, the importance of organic matter pathways in the relocation of TEs along the whole food web is poorly investigated, limiting the ability to predict how variations in sea-ice dynamics and primary production due to climate change will affect TE transfer across species and trophic levels.

Owing to the robustness of stable isotopes ($\delta^{13}C$ and $\delta^{13}N$) and Bayesian mixing models in the identification of basal sources of dietary carbon, and the trophic level of organisms in food webs (Costantini et al., 2018; Post, 2002; Rossi et al., 2015; Vizzini et al., 2016), such combined approach is highly suitable to evaluate the role of horizontal (i.e. reliance of consumers on different basal sources and trophic pathways) and vertical food web structure (i.e. trophic positions) in the TE transfer. In particular, as organic matter sources are typically well distinct based on $\delta^{13}C$ signatures (Costantini et al., 2014; Fry and Sherr, 1989; Signa et al., 2017b) especially in Antarctica (Norkko et al., 2007; Calizza et al., 2018), and consumers reflect the $\delta^{13}C$ of prey plus only a low fractionation value (0–1‰) (De Niro and Epstein, 1978; McCutchan et al., 2003), a positive or negative relationship between TEs and $\delta^{13}C$ of consumers will reveal the importance of the underlying $^{13}C$-enriched vs. $^{13}C$-depleted organic matter pathways in TE transfer from basal sources to consumers. In contrast, the positive or negative relationship between TEs and $\delta^{15}N$ of species across trophic levels indicates TE biomagnification or biodilution along food webs (e.g. Lavoie et al., 2013; Nfon et al., 2009; Signa et al., 2013).

In recent years, significant changes in sea ice extent and seasonal dynamics have been observed at the poles, leading to dramatic ecological consequences in productivity and trophic patterns (Post et al., 2013; Constable et al., 2014). As the sea ice thickness and seasonal melting are critical to ensure the subsequent timing of ice algal and phytoplankton blooms and their vertical distribution, the predicted changes in sea ice cover and thickness and the consequent shift in frequency, magnitude and availability of sympagic/planktonic production may propagate across trophic levels through bottom-up processes (Constable et al., 2014). Moreover, higher macroalgae abundance along the Antarctic coasts is also expected from climate change predictions (Clark et al., 2013), with cascade effects on the food web structure.

In this context, understanding the extent of TE transfer in the Antarctic food web, and disentangling how diet and organic matter pathways (benthic, pelagic or sympagic) drive the transfer of trace elements to the biota, is extremely important. Therefore, the main aim of this paper was to assess and identify the pathways of trace elements (Cd, Cr, Co, Cu, Hg, Ni, Pb, V) in the food web of Tethys Bay (Terra Nova Bay, Ross Sea, Antarctica). To do this, the food web structure and organic matter pathways were first characterised through stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) and Bayesian mixing models (Calizza et al., 2018; Norkko et al., 2007; Parnell et al., 2013). Then, the influence of the horizontal (i.e. reliance of consumers on different basal sources and trophic pathways) and vertical (i.e. trophic positions) food web structure in TE transfer to consumers was assessed through multivariate analysis and linear regressions between TEs, $\delta^{13}C$, and $\delta^{15}N$. This also allowed to quantify the trophic magnification factor (TMF) for each element, which was useful to describe biomagnification or biodilution across trophic levels. We hypothesised that i) pelagic and sympagic primary producers, namely phytoplankton and sea-ice algae, play an important role in

the TE transfer to primary consumers, with potential repercussions in the contamination level of top predators, ii) diet and trophic position are also important drivers for TE transfer to upper trophic levels of the food web of Tethys Bay, in the Ross Sea.

## 2. Materials and methods

### 2.1. Study area and sampling

Sampling was performed at Tethys Bay, (Terra Nova Bay, Ross Sea, Antarctica) (74°41'40"S 164°03'22"E), at the end of January 2013 (austral summer). The bay extends 3 km from the inner to the outer limit and is connected to the open waters of the polynya of Terra Nova Bay. The seafloor is characterised by rocky and muddy patches, and benthic vegetation coverage is generally scarce. Evident sea-ice cracking and melting in the bay started ten days before sampling. Sea-ice coverage and primary productivity in the bay are characterised by marked seasonality, with periods of complete absence of ice coverage and phytoplankton blooms typically observed in January. Further information on the study area can be found in Faranda et al. (2000) and Norkko et al. (2007).

Methods for basal source and invertebrate collection are reported in Calizza et al. (2018). Briefly, benthic invertebrates were sampled along linear transects by dredging in medium-depth waters (~40−200 m) and by scuba diving in shallow waters (15−25 m). Fish were collected through fish lines and creels which allowed to sample both the benthic habitat and the water column. Bird feathers of adult Adélie penguins and skua (*Stercorarius antarcticus*) were collected by hand from recently died organisms. Resources potentially contributing to the diet of primary and secondary consumers were also collected by dredging and scuba diving in deep and shallow waters respectively, including (i) benthic organic matter sources [sediment and coarse (>2 mm) organic detritus] and primary producers (the red macroalgae *Iridaea cordata* and *Phyllophora antarctica*); (ii) planktonic primary producers and consumers (respectively phytoplankton and zooplankton) were collected with a plankton net (20 μm mesh size) until a depth of 100 m. Zooplankton was carefully separated from the rest of the bulk sample by hand under a stereoscope. To obtain phytoplankton, the remaining sample was prefiltered at 100 μm and then collected on pre-combusted Whatmann GF/F filters; (iii) sympagic primary producers (microscopic algae and filamentous aggregates growing within the ice and at the interface between sea-ice and water) were collected in November 2012, before sea-ice broke up, by coring the pack-ice at two sites in the inner and outer part of the bay. Interface algae (i.e. the 2 cm bottom layer of the core) were considered separately from those growing within the core (i.e. between 2 cm and 1 m from the bottom, hereafter "core algae").

### 2.2. Laboratory activities

For both isotopic and trace element (TE) analysis, soft tissues of all invertebrate and vertebrate species/taxa ranging across trophic levels and trophic guilds were considered (Table S1). All samples were stored at −80 °C at the "Mario Zucchelli" Italian Research Station, and at −20 °C during transportation to Italy, where, after freeze-drying, they were ground using a ball mill (Mini-Mill Fritsch Pulverisette 23: Fritsch Instruments, Idar-Oberstein, Germany).

#### 2.2.1. Isotopic analysis

When necessary, samples were pre-acidified (HCl 1 M) to eliminate inorganic carbon, which can interfere with the $\delta^{13}C$ signature (Carabel et al., 2006). Un-acidified powder from each sample was also analysed for the $\delta^{15}N$ signature, which is affected by HCl exposure (Carabel et al., 2006). Then, samples underwent

stable isotope analysis (SIA) by means of an IRMS (IsoPrime100, Isoprime Ltd., Cheadle Hulme, UK) coupled with an EA (Elementar Vario Micro-Cube, Elementar Analysensysteme GmbH, Germany). Each sample was analysed in two replicates, and isotopic signatures were expressed in δ units (δ$^{13}$C; δ$^{15}$N) as the per mil (‰) difference with respect to standards: δ$^X$ (‰) = [(R$_{sample}$ - R$_{standard}$)/R$_{standard}$] x 10$^3$, where X is $^{13}$C or $^{15}$N and R is the corresponding ratio of heavy to light isotopes ($^{13}$C/$^{12}$C or $^{15}$N/$^{14}$N) (Post, 2002). The reference materials used were the international Vienna PeeDee Belemnite (PDB) for carbon, and atmospheric nitrogen (N$_2$) for nitrogen. Measurement errors were found to be typically smaller than 0.1‰. For δ$^{13}$C, outputs were corrected for lipid content (Post et al., 2007) based on the C/N ratio (not reported) of each sample.

### 2.2.2. Trace element analysis

For quantification of trace elements (TEs: Cd, Co, Cr, Cu, Hg, Ni, Pb and V), ground samples were mineralised in a microwave system (MARS 5, CEM): sediment was analysed using a solution of 67–70% HNO$_3$, 30% HF, 30% H$_2$O$_2$ and Milli-Q water, while biological tissues using 67–70% HNO$_3$, 30% H$_2$O$_2$, and Milli-Q water. Then, mineralised samples were analysed by ICP-OES (Optima 8000, PerkinElmer). Concentrations of Hg were determined using a hydride generation system linked to the ICP-OES with a reductant, consisting of 0.2% sodium (Na) borohydride and 0.05% Na hydroxide.

Analytical quality control was performed using Certified Reference Materials (CRMs): Marine sediment NIST-2702 (National Institute of Standards and Technology) for sediments, *Lagarosiphon major* BCR–060 (Institute for Reference Materials and Measurements) for primary producers, Fish protein DORM-4 (National Research Council of Canada) for vertebrates and Oyster tissue NIST-1566b for invertebrates. The recovery was 84–101%. The detection limit was calculated as three times the standard deviation for digestion blanks (n > 20) and was similar for all analysed TEs, corresponding to 0.003 mg kg$^{-1}$ dw. All results are given in mg kg$^{-1}$ dw.

### 2.3. Data elaboration and statistics

The biotic samples analysed were grouped into eight categories (Table S1). In detail, organic matter sources were grouped in: sediment (SED) including sedimentary organic matter and detritus; sympagic algae (SYMP) including core and interface sea-ice algae; phytoplankton (PHYTO-P); phytobenthos (PHYTO-B) including *I. cordata* and *P. antarctica*. Consumers were grouped in: zooplankton (ZOO-P) including *Clione limacina* (Gastropoda), copepods and *Euphasia* sp.; zoobenthos (ZOO-B) including the invertebrates *Adamussium colbecki* (Bivalvia), *Odontaster validus* (Asteroidea), *Sterechinus neumayeri* (Echinoidea), *Ophionotus victoriae* (Ophiuroidea), *Haliclona* sp. (Demospongiae), Cucumaridae (Holoturoidea), Alcyonacea (Anthozoa) and Polychaeta; fish (FISH) including *Artedidraco orianae*, *A. skottsbergi*, *Chionodraco hamatus*, *Lepidonotothen nudifrons*, *Trematomus bernacchii*, *T. hansoni*, *T. newnesi* and *T. pennellii*; and birds (BIRDS) including the penguin *Pygoscelis adeliae* and the Antarctic Skua *Stercorarius antarcticus*. Analyses focused on these targets because they are among the most common taxa within their respective trophic guilds in the study area and in Antarctic coastal communities.

Differences in the isotopic values among categories were tested by means of a non-parametric MANOVA (NPMANOVA) based on Euclidean distances (Calizza et al., 2017, 2013) followed by post-hoc tests. The significance is computed by permutation of group membership, with 10000 replicates. Differences in trace elements (TE) concentration between the eight categories were tested through permutational analysis of variance (PERMANOVA) carried out for each TE based on the Euclidean distance matrix obtained by

normalised TE data, followed by pairwise tests.

Isotopic Bayesian mixing models (SIAR, Parnell et al., 2013) were run to describe the diet of zoobenthos and zooplankton. This was not achieved for fish and birds, given that some of their potential prey were missing from the dataset. The SIAR model required three inputs: the isotopic signatures of the target consumers and their potential food sources (as mean and standard deviation for each source), and the Trophic Enrichment Factor (TEF), i.e. the isotopic difference between a consumer and its diet. Here, a TEF value of δ$^{15}$N: 2.3 ± 0.4‰, and δ$^{13}$C: 0.4 ± 0.2‰ was applied. Based on a broad literature analysis by McCutchan et al. (2003), these values produced meaningful mixing model outputs when applied to benthic invertebrates in our study area (Calizza et al., 2018; Norkko et al., 2007). Then, based on diet composition, the trophic position (TP) of each taxon in the food web was calculated in accordance with the formula:

$$TP_i = 1 + \Sigma_j (TP_j * f_{ij})$$

where TP$_j$ is the trophic position of prey j, and f is the proportional consumption of prey j by predator i (Odum and Heald, 1975). Basal food sources were assigned to a TP = 1. In addition, for each taxon, the contributions of resources/prey belonging to different categories were also summed together and compared. Given the strong and linear correlation between δ$^{15}$N and TPs in those taxa where diets were described (see Results), the TP of fish was estimated starting from the individual δ$^{15}$N measured in organisms. This was possible because TEF values in Antarctic fish (TEF: δ$^{15}$N: 2.1 ± 0.7‰, δ$^{13}$C: 0.4 ± 0.2‰) are highly similar to those generally expected in invertebrates and applied here (McMullin et al., 2017).

A Mantel test was applied to assess if (i) isotopic signatures of taxa were predictive of diet composition, and (ii) TE concentrations in organisms were dependent on their diet composition. The Mantel test is a permutation test for correlation between two distance or similarity matrices (Mantel, 1967; Mantel and Valand, 1970) and allows to compare multivariate data with different similarity measures. Here, the Euclidean distance, the Bray-Curtis dissimilarity, and the Mahalanobis distance (a distance measure taking into account the covariance structure of the data) were selected to quantify isotopic distances between taxa, pairwise differences in diets, and dissimilarity in TE concentrations between taxa respectively (Calizza et al., 2017).

The effect of the horizontal and vertical food web structure (i.e. organic matter pathways and trophic position) in shaping the TE pathways within the Antarctic food web was also assessed through linear regressions between the logarithm of TEs as the dependent variable and δ$^{13}$C and δ$^{15}$N as independent variables. In the first case (log[TE] vs. δ$^{13}$C), the role of primary producers and sediment as TE sources was tested separately for primary and secondary consumers to distinguish potentially different patterns. In the second case (log[TE] vs. δ$^{15}$N), all the biotic samples, except for bird feathers, were included to assess the biomagnification/biodilution patterns along the food web. Feathers were excluded to avoid any potential bias due to the different dynamics of TE accumulation and stable isotope fractionation between internal and external tissues (Brasso et al., 2014; Pedro et al., 2015). Residual analysis was performed in both regression analyses to ensure that assumptions were not violated. If outliers were identified, they were removed and the regression analysis was performed again. Trophic magnification factors (TMF) were also calculated from the slope of the regression of log[TE] vs. δ$^{15}$N (TMF = 10$^{b*2.3}$) and vs. trophic position TP (TMF = 10$^b$) according to Lavoie et al. (2013) to quantify the biomagnification (TMF>1) or biodilution (TMF<1) power of the TEs along the food web. The constant 2.3 (‰) is the TEF value applied in this study, accounting for the δ$^{15}$N increase per trophic level.
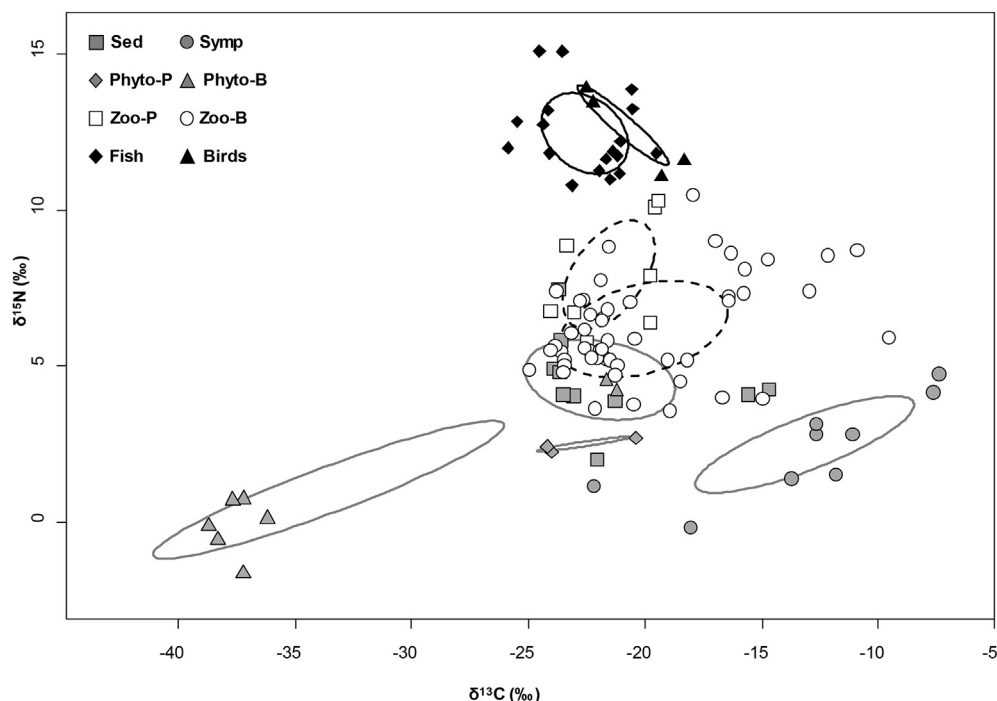
**Fig. 1.** Isotopic distributions of different basal sources (grey symbols), invertebrate (white symbols) and vertebrate (black symbols) taxa at Tethys Bay, Ross Sea (Antarctica). Different symbols represent different categories and each symbol represents a specimen. Ellipses encompass the core (i.e. 46%) of each categories.

## 3. Results

### 3.1. Isotopic signatures and diets

Isotopic distribution differed between all groups analysed (NPMANOVA $F = 30.2$, $p < 0.0001$; associated post-hoc tests: $p < 0.05$ always) (Table S2), with the exception of fish and birds, which did not differ significantly ($p > 0.05$). Specifically, isotopic distributions of the four main basal resource guilds (i.e. sediment, phytobenthos, phytoplankton and sympagic algae) differed either for their $\delta^{13}C$ or $\delta^{15}N$ values (Fig. 1). Basal resources occupied a $\delta^{13}C$ range much wider than consumers which, in turn, mainly differed for their $\delta^{15}N$ values.

Basal food sources provided a different proportional contribution to the diet of benthic taxa (Fig. 2, one-way ANOVA for repeated measures, $F = 3.5$, $p < 0.01$, see Table S3 for details). Sympagic algae were the most assimilated food source ($37 \pm 4\%$), followed by sediment and phytoplankton ($14 \pm 3\%$ and $18 \pm 4\%$ respectively). As regards omnivorous benthic consumers (i.e. *Sterechinus neumayeri*, *Odontaster validus*, *Ophionotus victoriae* and polychaetes), animal prey also provided a relevant contribution ($44 \pm 10\%$). In parallel, pelagic and sympagic sources both contributed to the diet of zooplankton (Fig. 2). Overall, the isotopic distances between taxa significantly reflected differences in the composition of their diets (Mantel test, $R = 0.46$, $p = 0.01$). Also, the trophic positions of invertebrate taxa linearly increased with their $\delta^{15}N$ values
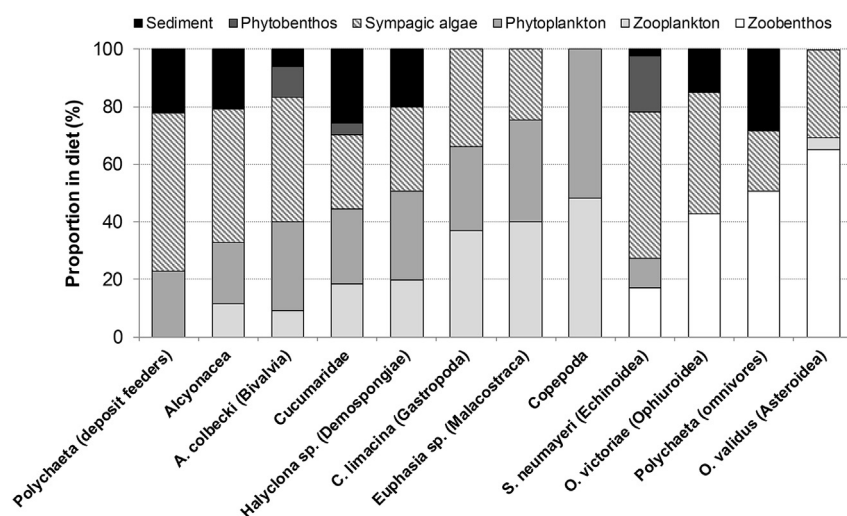


**Fig. 2.** Percentage contribution of different resource categories to the diet of invertebrate Antarctic taxa at Tethys Bay (Ross Sea). The diet of each taxon was described in detail by means of Bayesian isotopic mixing models (see Table S3). Then, contributions of resource items belonging to the same resource category were summed together.

$(y = 2.8261x-0.5397, \quad r = 0.93, \quad p < 0.0001, \quad p \text{ against permutation} = 0.001)$, allowing to estimate the TP of remaining taxa starting from individual isotopic values (Table S1).

## 3.2. Trace elements

Trace element (TE) analysis revealed different patterns among sample categories and TEs (Fig. 3). Cr, Ni, Pb and V showed similar trends, with overall significantly higher concentrations in organic matter sources than consumers. In particular, Cr peaked in phytoplankton, followed by sediment and sea-ice algae, while benthic macroalgae reported similar concentrations to zooplankton and birds. In contrast, Ni, Pb and V showed the highest concentration in phytoplankton and sediment, followed by sea-ice algae and benthic macroalgae, which showed values comparable to birds and zooplankton (Ni, Pb) and zoobenthos (V). Cu concentration in phytoplankton was also high, but the highest values were recorded in sea-ice algae. The remaining source and consumer categories highlighted similar lower values with the lowest ones recorded in fish. Co concentration peaked in sediment, followed by all the other categories with evenly lower values. In contrast, Hg levels were significantly higher in birds than in all the other categories, among which fish showed the highest concentration, followed by benthic invertebrates, sea-ice algae and phytoplankton as an homogeneous group. Finally, Cd did not show a clear trend and the highest values were observed in benthic invertebrates, phytoplankton and phytobenthos, followed by zooplankton and sea-ice algae.

Overall, concentrations of TE measured in invertebrate taxa were significantly associated with both their isotopic signatures and diet composition, i.e. the more similar the isotopic values and diets between two taxa, the more similar TEs' identity and concentration in their tissues (Mantel tests, $R = 0.33$ and $p = 0.02$ in both cases).

In primary consumers, Pb and V were negatively and positively correlated, respectively, with $\delta^{13}C$, while in secondary consumers the correlation was significant and positive for Cd and Hg, and negative for Pb (Fig. 4; Table 1). Pb decreased along $\delta^{13}C$ in both primary and secondary consumers, while Cd and Hg decreased in primary consumers and increased in secondary consumers (Fig. 4).

Linear regressions between log[TE] and $\delta^{15}N$ of the food web components (except birds), highlighted a similar behaviour of all TEs, except for log[Hg] (Fig. 5; Table 2). Indeed, the log[TE] significantly decreased as the $\delta^{15}N$ increased, indicating TE biodilution along the food web, while only log[Hg] significantly increased along $\delta^{15}N$ values, suggesting Hg biomagnification across trophic levels (Fig. 5). These patterns were confirmed by the trophic magnification factor (TMF), which was lower than 1 for all TEs except for Hg (Table 2). Comparison of the results of the regressions performed using $\delta^{15}N$ and trophic position (TP) as independent variables indicated the same patterns but different ranges of variation: TMF ranged between 0.54 and 1.44 when based on regressions between log[TE] and $\delta^{15}N$, and from 0.38 to 1.69 when based on regressions between log[TE] and TP (Table 2).

## 4. Discussion

### 4.1. Food web structure

Isotopic values of the organic matter sources from Tethys Bay, Ross Sea (Antarctica) covered a wide $\delta^{13}C$ range ($\Delta^{13}C = 31.2‰$) varying from the highly depleted red macroalga *Phyllophora antarctica*, to the highly enriched sympagic algae. The benthic red macroalga *Iridaea cordata*, phytoplankton and sediment showed intermediate values. The large differences in $\delta^{13}C$ signatures among primary producers is not new in Antarctica and current results are consistent with previous studies (Gillies et al., 2012; Norkko et al., 2007; Calizza et al., 2018). Overall, the horizontal food web structure of Tethys Bay was characterised by two main trophic pathways, the first based on sympagic algae and the second on phytoplankton. The sedimentary pathway was important only for some benthic
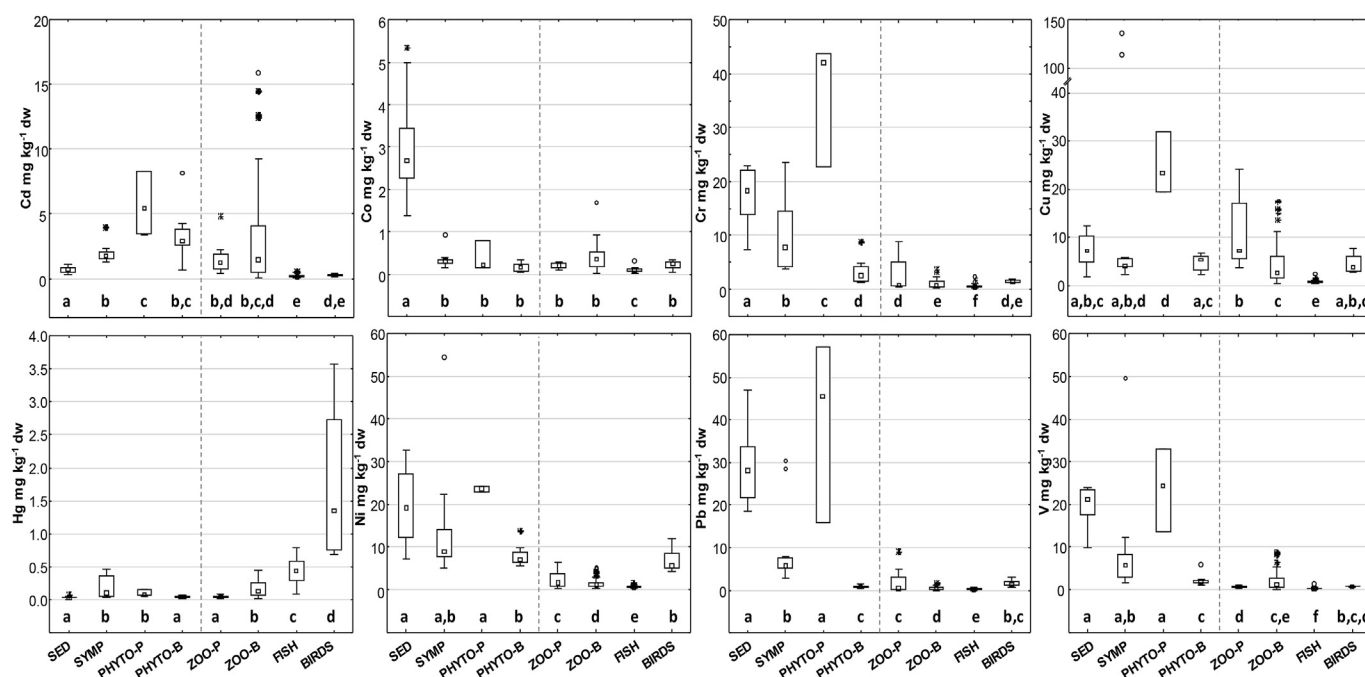


**Fig. 3.** Trace element concentrations (mg kg$^{-1}$ dw) in organic matter sources: sediment organic matter (SED); sympagic algae (SYMP); phytoplankton (PHYTO-P) and phytobenthos (PHYTO-B), and in consumers: zooplankton (ZOO-P); zoobenthos (ZOO-B); fish (FISH) and birds (BIRDS) from Tethys Bay, Ross Sea (Antarctica). Whiskers indicate the non-outlier range of variation; boxes: 25th to 75th percentiles. Significant differences among sample categories are indicated with different letters.
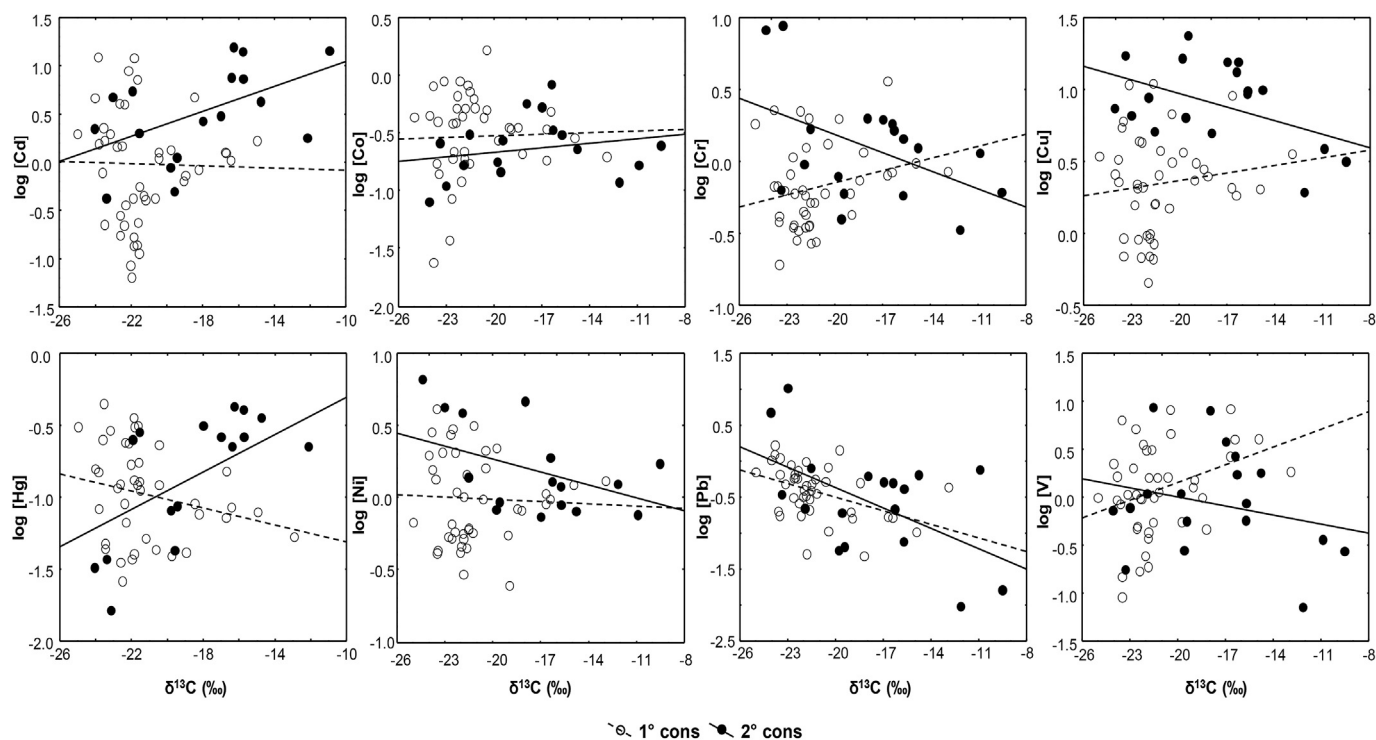
**Fig. 4.** Linear regressions for log-transformed trace element (TE) concentrations (mg kg$^{-1}$ dw) vs. δ$^{13}$C (‰) signatures of primary consumers in white, and secondary consumers in black, from Tethys Bay, Ross Sea (Antarctica). Regression equations and parameters (r and p-values) are reported in Table 1.

**Table 1**
Results of linear regressions (equation, coefficient of regression r, and p value) between log-transformed concentration of trace elements and δ$^{13}$C (primary and secondary consumers).

| TE | [log TE] vs. δ$^{13}$C- 1° consumers | | | [log TE] vs. δ$^{13}$C - 2° consumers | | |
|---|---|---|---|---|---|---|
| | equation | r | p | equation | r | p |
| **Cd** | y = - 0.0119x - 0.0934 | 0.01 | 0.96 | y = 0.0637x + 1.6702 | 0.51 | **< 0.05** |
| **Co** | y = 0.0057x - 0.3793 | 0.04 | 0.80 | y = 0.0138x - 0.3691 | 0.22 | 0.37 |
| **Cr** | y = 0.0385x + 0.4339 | 0.25 | 0.12 | y = - 0.0393x - 0.6034 | 0.43 | 0.07 |
| **Cu** | y = 0.0183x + 0.7353 | 0.14 | 0.38 | y = - 0.03x + 0.3913 | 0.44 | 0.06 |
| **Hg** | y = - 0.0348x - 1.7051 | 0.28 | 0.08 | y = 0.0613x + 0.2723 | 0.57 | **< 0.05** |
| **Ni** | y = - 0.049x - 0.1211 | 0.04 | 0.79 | y = - 0.0279x - 0.3216 | 0.38 | 0.13 |
| **Pb** | y = - 0.0612x - 1.7112 | 0.43 | **< 0.05** | y = - 0.0958x - 2.2383 | 0.54 | **< 0.05** |
| **V** | y = 0.0607x + 1.3699 | 0.33 | **< 0.05** | y = - 0.03x - 0.5733 | 0.23 | 0.36 |

invertebrates, while phytobenthos was by far the less exploited organic matter source, plausibly because of the abundance of polyphenols that protect it from grazers (Norkko et al., 2007; Calizza et al., 2018). These results can be better explained when considering that our sampling occurred in the summer period, when the high availability of pelagic production and deposited sympagic material allows invertebrate consumers to specialise on these temporally abundant food sources (Calizza et al., 2018; Norkko et al., 2007; Wing et al., 2018).

Benthic invertebrates included both primary and secondary consumers with a greater contribution of sympagic algae, sediment and phytoplankton in the diet of the former, and a greater contribution of zoobenthos in the diet of the latter. Indeed, Antarctic benthic invertebrates can vary greatly in their feeding habits (Corbisier et al., 2004), and exhibit a high degree of trophic plasticity and omnivory (Norkko et al., 2007). In parallel, zooplankton relied mainly on phytoplankton and sympagic algae, as well as on other planktivorous copepods, showing an omnivorous feeding strategy (Tamelander et al., 2008). Lastly, the highest TP and δ$^{15}$N of

fish and birds and their intermediate position within the δ$^{13}$C range, highlight the role as top predators that couple the underlying resource pathways, as previously documented in Arctic (McMeans et al., 2013) and temperate marine systems (Vizzini et al., 2016).

### 4.2. Trace element levels in food web components

Sediment trace element (TE) concentration measured in this study was overall comparable to previous studies in the Ross Sea (Grotti et al., 2008; Ianni et al., 2010), with the exception of Pb and Hg, which showed higher values compared with existing literature (Pb: Grotti et al., 2008; Ianni et al., 2010; Hg: Bargagli et al., 1998; Negri et al., 2006). The elevated pelagic primary productivity of the Antarctic system (Petrou et al., 2016), together with the high TE levels in the dissolved compartment (Corami et al., 2005; Sañudo-Wilhelmy et al., 2002), explain the important role of phytoplankton within the food web and also its enrichment in TEs, thus representing a potential source of TEs for both pelagic and benthic consumers (once settled on the seafloor) (Cabrita et al., 2017;
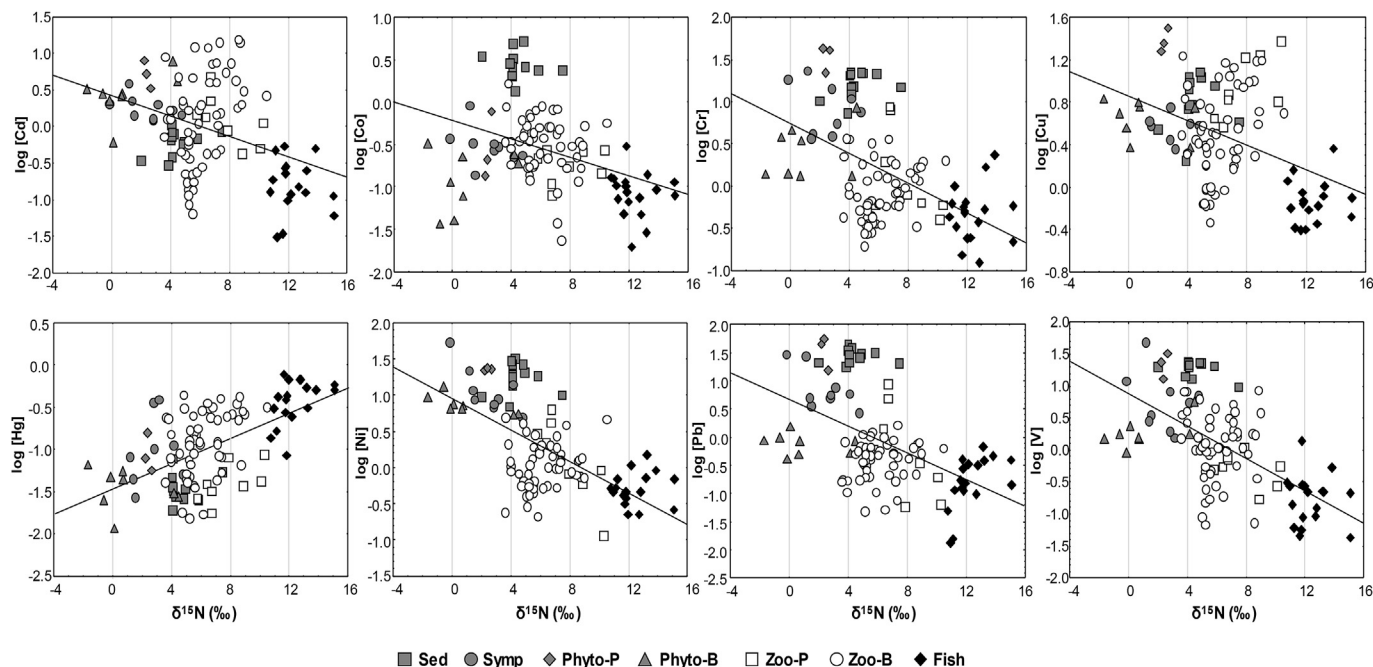
**Fig. 5.** Linear regressions for log-transformed trace element (TE) concentrations (mg kg$^{-1}$ dw) vs. $\delta^{15}$N (‰) signatures of the whole food web of Tethys Bay, Ross Sea (Antarctica), with the exception of birds. Regression equations and parameters (r and p-values), and TMF are reported in Table 2.

**Table 2**
Results of linear regressions (equation, coefficient of regression r, and p value) between log-transformed concentration of trace elements and both $\delta^{15}$N and trophic position TP. Trophic magnification factors TMF are also reported for both relations.

| TE | log [TE] vs. δ15N | | | | log [TE] vs. TP | | | |
|---|---|---|---|---|---|---|---|---|
| | equation | r | p | TMF ($10^{b*2.3}$) | equation | r | p | TMF ($10^b$) |
| **Cd** | y = − 0.0698x + 0.4177 | 0.40 | **< 0.001** | 0.69 | y = −0.1862x + 0.4199 | 0.37 | **< 0.001** | 0.65 |
| **Co** | y = − 0.0593x −0.2022 | 0.38 | **< 0.001** | 0.75 | y = −0.2158x − 0.0309 | 0.54 | **< 0.001** | 0.61 |
| **Cr** | y = − 0.0893x + 0.749 | 0.50 | **< 0.001** | 0.62 | y = −0.3098x + 0.9072 | 0.61 | **< 0.001** | 0.49 |
| **Cu** | y = − 0.057x + 0.8567 | 0.42 | **< 0.001** | 0.74 | y = −0.1735 + 0.9072 | 0.46 | **< 0.001** | 0.67 |
| **Hg** | y = 0.0758x - 1.4485 | 0.58 | **< 0.001** | 1.49 | y = 0.22275x - 1.5097 | 0.62 | **< 0.001** | 1.69 |
| **Ni** | y = − 0.1098x + 0.9706 | 0.62 | **< 0.001** | 0.56 | y = −0.3453x + 1.0973 | 0.69 | **< 0.001** | 0.45 |
| **Pb** | y = − 0.1164x + 0.6548 | 0.50 | **< 0.001** | 0.54 | y = −0.4099x + 0.8918 | 0.62 | **< 0.001** | 0.39 |
| **V** | y = − 0.1262x + 0.9241 | 0.61 | **< 0.001** | 0.51 | y = −0.4215x + 1.1264 | 0.71 | **< 0.001** | 0.38 |

Deheyn et al., 2005). Similarly, sympagic algae, which are bioavailable in summer as soon as the pack-ice starts to melt (Grotti et al., 2005, Pusceddu et al., 2009), are good bioaccumulator of nutrients and TEs. This is confirmed by present results. Indeed, phytoplankton and sympagic algae showed overall the highest TE concentrations among basal sources. In particular, phytoplankton reached TEs levels from 2-fold (Hg) to 4- (Cd) and even 10-fold (Pb) higher than those previously recorded in the same area (Bargagli et al., 1998, 1996; Cabrita et al., 2017; Dalla Riva et al., 2003).

As regards consumers, only Cd, Cu and Hg revealed remarkable TE concentrations. High Cd levels in both primary producers and invertebrates were already observed in Terra Nova Bay by Bargagli et al. (1996) who defined it as "the Cd anomaly", due to the up-welling of Cd-enriched deep waters. Copper showed accumulation patterns similar to Cd, consistently with the findings by Grotti et al. (2008), while the Hg pattern suggests biomagnification, as previously documented in the area (Bargagli et al., 1998) and in other polar and temperate systems (Nfon et al., 2009; Signa et al., 2017c). Consistently with previous observations (Becker et al., 2016), the highest Hg levels were found in bird feathers, especially in those of the skua (*Stercorarius antarcticus*).

### 4.3. Horizontal and vertical food web structure drives trace element transfer

Linear regressions between consumer log[TE] and $\delta^{13}$C highlighted that the sympagic pathway was not relevant in driving TE transfer to primary consumers, unless for V. In contrast, the significant and positive correlation between both log[Cd] and log[Hg] vs. $\delta^{13}$C revealed the importance of this pathway in the transfer of Cd and Hg up to secondary consumers. Such not consistent Cd and Hg pattern between primary and secondary consumers may depend on the conjoint key role of benthic and sympagic pathway in conveying these two elements to benthic primary consumers. Indeed, the taxa grouped in the upper right part of the graphs (i.e. mainly *Haliclona*, sp., cucumaridae and the deposit feeder polychaetes, Fig. 4), also showed a high reliance on sediment as organic matter source. Therefore, we can infer that secondary consumers showed high Cd and Hg levels derived from the two pathways combined due to their omnivorous feeding behaviour (Norkko et al., 2007). Although many Antarctic benthic and pelagic consumers are active predators/scavengers (Dalla Riva et al., 2004), the direct reliance of omnivores on sea-ice algae has also been

observed following the sympagic fallout associated to seasonal sea-ice melting (Morata et al., 2011; Wing et al., 2018). This is consistent with the assimilation of sea-ice algae measured here in omnivorous benthic invertebrates, further highlighting the complexity of TE transfer pathways in Antarctic benthic communities.

In contrast with remaining elements, Pb was the only element that significantly decreased as the $\delta^{13}$C increased. This was observed both in primary and secondary consumers, suggesting that phytoplankton and sediment represented the main Pb sources for invertebrates in Tethys Bay. Lead is defined as a "scavenging type" element that typically shows increasing concentration at higher depths (Frache et al., 2001; Illuminati et al., 2017). Illuminati et al. (2017) found that the sinking of biogenic particles following the phytoplankton bloom affects the Pb level in the deeper layers (~100 m - same maximum depth where the phytoplankton was sampled in this study). Our results, in agreement with literature findings (Elias-Piera et al., 2013; Norkko et al., 2007), support the hypothesis that sediment and phytodetritus can be relevant organic matter sources in the food web of Tethys Bay. Similarly, the pelagic pathway seems to have a relevant role in conveying Cr and Cu to secondary consumers, as indicated by the correlation between their concentrations and $\delta^{13}$C values in organisms. As regards Co and Ni, for which any clear pattern was identified, it could be argued that a conjoint contribution of all sources in the TE transfer to consumers takes place, rather than having no role in TE transfer. Notably, a multivariate analysis (i.e. the Mantel test) showed that similarity in element concentrations among benthic taxa was predicted by their similarity in diet composition, further suggesting that exposure to trace elements in the Antarctic food web is a complex process, which could not be fully clarified by the analysis of single trophic pathways.

Linear regression between trace elements and both $\delta^{15}$N and trophic positions were highly significant for all the elements analysed. However, only total mercury (Hg) biomagnified along the food web of Tethys Bay. The values of the slope and TMF were consistent with the lower values published, due to the use of total Hg, instead of Me−Hg, and the large variety of trophic levels studied here (Signa et al., 2017c), in contrast to most bio-magnification studies, which often focused on a subset of species and trophic levels. In Terra Nova Bay, Bargagli et al. (1998) were the first to describe such Hg behaviour, taking into account many organisms belonging to different trophic levels, from phytoplankton to penguins. Subsequent studies confirmed this trend (Cipro et al., 2017), while focusing only on a subset of species, such as benthic organisms (Pereira Majer et al., 2014) or penguins (Calle et al., 2015; Carravieri et al., 2013). Present results confirm that trophic position plays the key role in the Hg level and relocation in the food web, although other factors can contribute to differences in Hg concentration observed among organisms having a similar trophic position. Indeed, benthic fauna showed comparable isotopic signatures but higher Hg concentrations than zooplankton. This may be explained by the higher Hg exposure in the benthic vs. pelagic compartment, as Hg methylation and photodemethylation occur in sediments and seawater respectively, resulting in an increase (methylation) and decrease (photodemethylation) of Hg bioavailability (Goutte et al., 2015). Unlike Hg, all the other TEs (i.e. Cd, Cr, Co, Cu, Ni, Pb, V) showed a biodiluting behaviour along the food web. This is consistent with previous studies carried out both in polar (Nfon et al., 2009) and temperate areas (Signa et al., 2017c), which also showed similar TMF values, suggesting a univocal pattern, regardless of geographical area or seasonality. This common biodilution trend has been attributed to the efficient TE sequestration and/or excretion abilities of the organisms during the trophic transfer, concurrent with the growth dilution in the large-bodied species at high trophic levels. Cd deserves a mention

apart because the Antarctic "Cd anomaly" leads to very high Cd concentrations (Bargagli et al., 1996; Sañudo-Wilhelmy et al., 2002) and also because Cd is prone to bioaccumulate and may also bio-magnify in benthic invertebrates (Pereira Majer et al., 2014; Signa et al., 2017a). Accordingly, here, Cd concentration was very high in benthic invertebrates and very low in fish muscle and bird feathers. Although at a first glance this result may suggest a bio-dilution along trophic levels, the occurrence of Cd sequestration in other tissues, such as liver and kidney (Bargagli et al., 1996; Bustamante et al., 2003) may have led to this result.

## 5. Conclusions and future perspectives

Trace element (TE) contamination and transfer is a topic of paramount concern worldwide including the remote Antarctic region, because of the occurrence of natural and anthropogenic transport processes on local-to-global scales. Despite many TEs have been widely described in single components of the Antarctic food web, the pathways fueling TE transfer to the biota up to high trophic levels are poorly characterised. Here, in this first effort to describe the Cd, Cr, Co, Cu, Hg, Ni, Pb and V transfer pathways in Terra Nova Bay, we provide evidences of the importance of both sympagic and pelagic pathways, and trophic position, in driving the TE transfer to the biota. In particular, a significant influence of the sympagic pathway on the Cd and Hg levels of secondary consumers was highlighted. The sedimentary pathway was also relevant in the Cd and Hg transfer to primary consumers, while a combined sedimentary and phytodetrital pathway was relevant in the Pb transfer to all consumers. Hg was the only element whose concentration increased from basal sources to fish and that also bio-magnified along the food web. In agreement with most literature, all the other TEs biodiluted across trophic levels.

Concluding, climate change scenarios forecast a dramatic change in sea-ice extent and dynamics in polar areas (Constable et al., 2014; Post et al., 2013). In turn, this will produce important changes in frequency and magnitude of sympagic/pelagic production, with potential shifts in their relative contribution to the benthic communities (Clark et al., 2013; Constable et al., 2014). In this context, these data represent a useful reference of present baseline conditions in Terra Nova Bay (Ross Sea), and revealed that changes of trophic pathways could also lead to a change of TE transfer through the Antarctic food web. Indeed, in light of the marked efficiency of benthic macrofauna in the exploitation of pulsed food sources according to their availability (Calizza et al., 2018; Mäkelä et al., 2017; Norkko et al., 2007), our findings suggest that changes in food inputs fuelling the food web may rebound in unprecedented exposure of Antarctic species to TEs, in terms of different TE species and concentrations, than what experienced in the past.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2018.12.071.

## References

Bargagli, R., Monaci, F., Sanchez-Hernandez, J.C., Cateni, D., 1998. Biomagnification

of mercury in an Antarctic marine coastal food web. Mar. Ecol. Prog. Ser. 169, 65–76. https://doi.org/10.3354/meps169065.

Bargagli, R., Nelli, L., Ancora, S., Focardi, S., 1996. Elevated cadmium accumulation in marine organisms from Terra Nova bay (Antartica). Polar Biol. 16, 513–520. https://doi.org/10.1007/BF02329071.

Becker, P.H., Goutner, V., Ryan, P.G., Gonz, J., González-Solís, J., 2016. Feather mercury concentrations in Southern Ocean seabirds: variation by species, site and time. Environ. Pollut. 216, 253–263. https://doi.org/10.1016/j.envpol.2016.05.061.

Brasso, R.L., Chiaradia, A., Polito, M.J., Raya Rey, A., Emslie, S.D., 2014. A comprehensive assessment of mercury exposure in penguin populations throughout the Southern Hemisphere: using trophic calculations to identify sources of population-level variation. Mar. Pollut. Bull. 97, 408–418. https://doi.org/10.1016/j.marpolbul.2015.05.059.

Bustamante, P., Bocher, P., Chérel, Y., Miramand, P., Caurant, F., 2003. Distribution of trace elements in the tissues of benthic and pelagic fish from the Kerguelen Islands. Sci. Total Environ. 313, 25–39. https://doi.org/10.1016/S0048-9697(03)00265-1.

Cabrita, M.T., Padeiro, A., Amaro, E., dos Santos, M.C., Leppe, M., Verkulich, S., Hughes, K.A., Peter, H.U., Canário, J., 2017. Evaluating trace element bioavailability and potential transfer into marine food chains using immobilised diatom model species *Phaeodactylum tricornutum*, on King George Island, Antarctica. Mar. Pollut. Bull. 121, 192–200. https://doi.org/10.1016/j.marpolbul.2017.05.059.

Calizza, E., Careddu, G., Sporta Caputi, S., Rossi, L., Costantini, M.L., 2018. Time- and depth-wise trophic niche shifts in Antarctic benthos. PLoS One 13, 1–17. https://doi.org/10.1371/journal.pone.0194796.

Calizza, E., Costantini, M.L., Careddu, G., Rossi, L., 2017. Effect of habitat degradation on competition, carrying capacity, and species assemblage stability. Ecol. Evol. 7, 5784–5796. https://doi.org/10.1002/ece3.2977.

Calizza, E., Costantini, M.L., Carlino, P., Bentivoglio, F., Orlandi, L., Rossi, L., 2013. *Posidonia oceanica* habitat loss and changes in litter-associated biodiversity organization: a stable isotope-based preliminary study. Estuar. Coast Shelf Sci. 135, 137–145. https://doi.org/10.1016/j.ecss.2013.07.019.

Calle, P., Alvarado, O., Monserrate, L., Cevallos, J.M., Calle, N., Alava, J.J., 2015. Mercury accumulation in sediments and seabird feathers from the Antarctic Peninsula. Mar. Pollut. Bull. 91, 410–417. https://doi.org/10.1016/j.marpolbul.2014.10.009.

Carabel, S., Godínez-Domínguez, E., Verisimo, P., Fernandez, L., Freire, J., 2006. An assessment of sample processing methods for stable isotope analyses of marine food webs. J. Exp. Mar. Biol. Ecol. 336, 254–261. https://doi.org/10.1016/j.jembe.2006.06.001.

Carravieri, A., Bustamante, P., Churlaud, C., Cherel, Y., 2013. Penguins as bioindicators of mercury contamination in the Southern Ocean: birds from the Kerguelen Islands as a case study. Sci. Total Environ. 454–455, 141–148. https://doi.org/10.1016/j.scitotenv.2013.02.060.

Cipro, C.V.Z., Montone, R.C., Bustamante, P., 2017. Mercury in the ecosystem of admiralty bay , king George Island , Antarctica : occurrence and trophic distribution. Mar. Pollut. Bull. 114, 564–570. https://doi.org/10.1016/j.marpolbul.2016.09.024.

Clark, G.F., Stark, J.S., Johnston, E.L., Runcie, J.W., Goldsworthy, P.M., Raymond, B., Riddle, M.J., 2013. Light-driven tipping points in polar ecosystems. Global Change Biol. 19, 3749–3761. https://doi.org/10.1111/gcb.12337.

Constable, A.J., Melbourne-Thomas, J., Corney, S.P., Arrigo, K.R., Barbraud, C., Barnes, D.K.A., Bindoff, N.L., Boyd, P.W., Brandt, A., Costa, D.P., Davidson, A.T., Ducklow, H.W., Emmerson, L., Fukuchi, M., Gutt, J., Hindell, M.A., Hofmann, E.E., Hosie, G.W., Iida, T., Jacob, S., Johnston, N.M., Kawaguchi, S., Kokubun, N., Koubbi, P., Lea, M.A., Makhado, A., Massom, R.A., Meiners, K., Meredith, M.P., Murphy, E.J., Nicol, S., Reid, K., Richerson, K., Riddle, M.J., Rintoul, S.R., Smith, W.O., Southwell, C., Stark, J.S., Sumner, M., Swadling, K.M., Takahashi, K.T., Trathan, P.N., Welsford, D.C., Weimerskirch, H., Westwood, K.J., Wienecke, B.C., Wolf-Gladrow, D., Wright, S.W., Xavier, J.C., Ziegler, P., 2014. Climate change and Southern Ocean ecosystems I: how changes in physical habitats directly affect marine biota. Global Change Biol. 20, 3004–3025. https://doi.org/10.1111/gcb.12623.

Corami, F., Capodaglio, G., Turetta, C., Soggia, F., Magi, E., Grotti, M., 2005. Summer distribution of trace metals in the western sector of the Ross Sea, Antarctica. J. Environ. Monit. 7, 1256–1264. https://doi.org/10.1039/b507323p.

Corbisier, T.N., Petti, M.A.V., Skowronski, R.S.P., Brito, T.A.S., 2004. Trophic relationships in the nearshore zone of martel inlet (king George Island, Antarctica): δ13C stable-isotope analysis. Polar Biol. 27, 75–82. https://doi.org/10.1007/s00300-003-0567-z.

Costantini, M.L., Calizza, E., Rossi, L., 2014. Stable isotope variation during fungal colonisation of leaf detritus in aquatic environments. Fungal Ecol 11, 154–163. https://doi.org/10.1016/j.funeco.2014.05.008.

Costantini, M.L., Carlino, P., Calizza, E., Careddu, G., Cicala, D., Sporta Caputi, S., Fiorentino, F., Rossi, L., 2018. The role of alien fish (the centrarchid *Micropterus salmoides*) in lake food webs highlighted by stable isotope analysis. Freshw. Biol. 63, 1130–1142. https://doi.org/10.1111/fwb.13122.

Dalla Riva, S., Abelmoschi, M.L., Chiantore, M., Grotti, M., Magi, E., Soggia, F., 2003. Biogeochemical cycling of Pb in the coastal marine environment at Terra Nova bay, Ross Sea. Antarct. Sci. 15, 425–432. https://doi.org/10.1017/S0954102003001524.

Dalla Riva, S., Abelmoschi, M.L., Magi, E., Soggia, F., 2004. The utilization of the antarctic environmental specimen bank (BCAA) in monitoring Cd and Hg in an antarctic coastal area in Terra Nova bay (Ross Sea - Northern Victoria land).

Chemosphere 56, 59–69. https://doi.org/10.1016/j.chemosphere.2003.12.026.

De Niro, M.J., Epstein, S., 1978. Influence of diet on the distribution of carbon isotopes in animals. Geochem. Cosmochim. Acta 42, 495–506. https://doi.org/10.1016/0016-7037(78)90199-0.

Deheyn, D.D., Gendreau, P., Baldwin, R.J., Latz, M.I., 2005. Evidence for enhanced bioavailability of trace elements in the marine ecosystem of Deception Island, a volcano in Antarctica. Mar. Environ. Res. 60, 1–33. https://doi.org/10.1016/j.marenvres.2004.08.001.

Elias-Piera, F., Rossi, S., Gili, J.M., Orejas, C., 2013. Trophic ecology of seven Antarctic gorgonian species. Mar. Ecol. Prog. Ser. 477, 93–106. https://doi.org/10.3354/meps10152.

Faranda, F.M., Guglielmo, L., Ianora, A., 2000. The Italian oceanographic cruises in the Ross Sea (1987–95): strategy, general considerations and description of the sampling sites. In: Ross Sea Ecology. Springer, Berlin Heidelberg, pp. 1–13.

Frache, R., Abelmoschi, M.L., Grotti, M., Ianni, C., Magi, E., Soggia, F., Capodaglio, G., Turetta, C., Barbante, C., 2001. Effects of ice melting on Cu, Cd and Pb profiles in Ross sea waters (Antarctica). Int. J. Environ. Anal. Chem. 79, 301–313. https://doi.org/10.1080/03067310108044391.

Fry, B., Sherr, E.B., 1989. δ13C measurements as indicators of carbon flow in marine and freshwater ecosystems. In: Rundel, P.W., Ehleringer, J.R., Nagy, K.A. (Eds.), Stable Isotopes in Ecological Research. Springer-Verlag, New York, pp. 196–229.

Gillies, C.L., Stark, J.S., Smith, S.D.A., 2012. Research article: small-scale spatial variation of δ13C and δ15N isotopes in Antarctic carbon sources and consumers. Polar Biol. 35, 813–827. https://doi.org/10.1007/s00300-011-1126-7.

Goutte, A., Cherel, Y., Churlaud, C., Ponthus, J.P., Massé, G., Bustamante, P., 2015. Trace elements in Antarctic fish species and the influence of foraging habitats and dietary habits on mercury levels. Sci. Total Environ. 538, 743–749. https://doi.org/10.1016/j.scitotenv.2015.08.103.

Grotti, M., Soggia, F., Ianni, C., Frache, R., 2005. Trace metals distributions in coastal sea ice of Terra Nova bay, Ross Sea, Antarctica. Antarct. Sci. 17, 289–300. https://doi.org/10.1017/S0954102005002695.

Grotti, M., Soggia, F., Lagomarsino, C., Dalla Riva, S., Goessler, W., Francesconi, K.A., 2008. Natural variability and distribution of trace elements in marine organisms from Antarctic coastal environments. Antarct. Sci. 20, 39–51. https://doi.org/10.1017/S0954102007000831.

Ianni, C., Magi, E., Soggia, F., Rivaro, P., Frache, R., 2010. Trace metal speciation in coastal and off-shore sediments from Ross Sea (Antarctica). Microchem. J. 96, 203–212. https://doi.org/10.1016/j.microc.2009.07.016.

Illuminati, S., Annibaldi, A., Romagnoli, T., Libani, G., Antonucci, M., Scarponi, G., Totti, C., Truzzi, C., 2017. Distribution of Cd, Pb and Cu between dissolved fraction, inorganic particulate and phytoplankton in seawater of Terra Nova Bay (Ross Sea, Antarctica) during austral summer 2011–12. Chemosphere 185, 1122–1135. https://doi.org/10.1016/j.chemosphere.2017.07.087.

Lavoie, R.A., Jardine, T.D., Chumchal, M.M., Kidd, K.A., Campbell, L.M., 2013. Biomagnification of mercury in aquatic food webs: a worldwide meta-analysis. Environ. Sci. Technol. 47, 13385–13394. https://doi.org/10.1021/es403103t.

Mäkelä, A., Witte, U., Archambault, P., 2017. Ice algae versus phytoplankton: resource utilization by Arctic deep sea macroinfauna revealed through isotope labelling experiments. Mar. Ecol. Prog. Ser. 572, 1–18. https://doi.org/10.3354/meps12157.

Mantel, N., 1967. The detection of disease clustering and a generalized regression approach. Cancer Res. 27, 209–220. https://doi.org/10.1038/214637b0.

Mantel, N., Valand, R.S., 1970. A technique of nonparametric multivariate analysis. Biometrics 26, 547–558.

McCutchan, J.H., Lewis, W.M., Kendall, C., Mcgrath, C.C., 2003. Variation in trophic shift for stable isotope ratios of carbon , nitrogen , and sulfur. Oikos 2, 378–390.

McMeans, B., Rooney, N., Arts, M., Fisk, A., 2013. Food web structure of a coastal Arctic marine ecosystem and implications for stability. Mar. Ecol. Prog. Ser. 482, 17–28. https://doi.org/10.3354/meps10278.

McMullin, R.M., Wing, S.R., Wing, L.C., Shatova, O.A., 2017. Trophic position of Antarctic ice fishes reflects food web structure along a gradient in sea ice persistence. Mar. Ecol. Prog. Ser. 564, 87–98. https://doi.org/10.3354/meps12031.

Morata, N., Poulin, M., Renaud, P.E., 2011. A multiple biomarker approach to tracking the fate of an ice algal bloom to the sea floor. Polar Biol. 34, 101–112. https://doi.org/10.1007/s00300-010-0863-3.

Negri, A., Burns, K., Boyle, S., Brinkman, D., Webster, N., 2006. Contamination in sediments, bivalves and sponges of McMurdo Sound, Antarctica. Environ. Pollut. 143, 456–467. https://doi.org/10.1016/j.envpol.2005.12.005.

Nfon, E., Cousins, I.T., Järvinen, O., Mukherjee, A.B., Verta, M., Broman, D., 2009. Trophodynamics of mercury and other trace elements in a pelagic food chain from the Baltic Sea. Sci. Total Environ. 407, 6267–6274. https://doi.org/10.1016/j.scitotenv.2009.08.032.

Norkko, A., Thrush, S.F., Cummings, V.J., Gibbs, M.M., Andrew, N.L., Norkko, J., Schwarz, A.M., 2007. Trophic structure of coastal antarctic food webs associated with changes in sea ice and food supply. Ecology 88, 2810–2820. https://doi.org/10.1890/06-1396.1.

Odum, W.E., Heald, E.J., 1975. The detritus-based food web of an estuarine mangrove communitye. In: Cronin, L.E. (Ed.), Estuarine Research, vol. 1. Academic Press, New York, NY, pp. 265–286.

Parnell, A.C., Phillips, D.L., Bearhop, S., Semmens, B.X., Ward, E.J., Moore, J.W., Jackson, A.L., Grey, J., Kelly, D.J., Inger, R., 2013. Bayesian stable isotope mixing models. Environmetrics 24, 387–399. https://doi.org/10.1002/env.2221.

Pedro, S., Xavier, J.C., Tavares, S., Trathan, P.N., Ratcliffe, N., Paiva, V.H., Medeiros, R., Vieira, R.P., Ceia, F.R., Pereira, E., Pardal, M.A., 2015. Mercury accumulation in

gentoo penguins *Pygoscelis papua*: spatial, temporal and sexual intraspecific variations. Polar Biol. 38, 1335–1343. https://doi.org/10.1007/s00300-015-1697-9.

Pereira Majer, A., Varella Petti, M.A., Navajas Corbisier, T., Portella Ribeiro, A., Theophilo, C.Y.S., Alves de Lima Ferreira, P., Lopes Figueira, R.C., 2014. Bioaccumulation of potentially toxic trace elements in benthic organisms of Admiralty Bay (King George Island, Antarctica). Mar. Pollut. Bull. 79, 321–325. https://doi.org/10.1016/j.marpolbul.2013.12.015.

Petrou, K., Kranz, S.A., Trimborn, S., Hassler, C.S., Blanco Ameijeiras, S., Sackett, O., Ralph, P.J., Davidson, A.T., 2016. Southern Ocean phytoplankton physiology in a changing climate. J. Plant Physiol. 203, 135–150. https://doi.org/10.1016/j.jplph.2016.05.004.

Post, D.M., 2002. Using stable isotopes to estimate trophic position: models, methods, and assumptions. Ecology 83, 703–718. https://doi.org/10.2307/3071875.

Post, D.M., Layman, C.A., Arrington, D.A., Takimoto, G., Quattrochi, J., Montaña, C.G., 2007. Getting to the fat of the matter: models, methods and assumptions for dealing with lipids in stable isotope analyses. Oecologia 152, 179–189. https://doi.org/10.1007/s00442-006-0630-x.

Post, E., Bhatt, U.S., Bitz, C.M., Brodie, J.F., Fulton, T.L., Hebblewhite, M., Kerby, J., Kutz, S.J., Stirling, I., Walker, D.A., 2013. Ecological consequences of sea-ice decline. Science (80-) 341, 519–525. https://doi.org/10.1126/science.1235225.

Pusceddu, A., Dell'Anno, A., Vezzulli, L., Fabiano, M., Saggiomo, V., Cozzi, S., Catalano, G., Guglielmo, L., 2009. Microbial loop malfunctioning in the annual sea ice at Terra Nova Bay (Antarctica). Polar Biol. 32, 337–346. https://doi.org/10.1007/s00300-008-0539-4.

Rossi, L., di Lascio, A., Carlino, P., Calizza, E., Costantini, M.L., 2015. Predator and detritivore niche width helps to explain biocomplexity of experimental detritus-based food webs in four aquatic and terrestrial ecosystems. Ecol. Complex. 23, 14–24. https://doi.org/10.1016/j.ecocom.2015.04.005.

Runcie, J.W., Riddle, M.J., 2004. Metal concentrations in macroalgae from East Antarctica. Mar. Pollut. Bull. 49, 1114–1119. https://doi.org/10.1016/j.marpolbul.2004.09.001.

Sañudo-Wilhelmy, S.A., Olsen, K.A., Scelfo, J.M., Foster, T.D., Flegal, A.R., 2002. Trace metal distributions off the antarctic peninsula in the Weddell sea. Mar. Chem. 77, 157–170. https://doi.org/10.1016/S0304-4203(01)00084-6.

Signa, G., Mazzola, A., Di Leonardo, R., Vizzini, S., 2017a. Element-specific behaviour and sediment properties modulate transfer and bioaccumulation of trace elements in a highly-contaminated area (Augusta Bay, Central Mediterranean Sea). Chemosphere 187, 230–239. https://doi.org/10.1016/j.chemosphere.2017.08.099.

Signa, G., Mazzola, A., Kairo, J., Vizzini, S., 2017b. Small-scale variability in geomorphological settings influences mangrove-derived organic matter export in a tropical bay. Biogeosciences 14, 617–629. https://doi.org/10.5194/bg-14-617-2017.

Signa, G., Mazzola, A., Tramati, C.D., Vizzini, S., 2017c. Diet and habitat use influence Hg and Cd transfer to fish and consequent biomagnification in a highly contaminated area: augusta Bay (Mediterranean Sea). Environ. Pollut. 230, 394–404. https://doi.org/10.1016/j.envpol.2017.06.027.

Signa, G., Tramati, C., Vizzini, S., 2013. Contamination by trace metals and their trophic transfer to the biota in a Mediterranean coastal system affected by gull guano. Mar. Ecol. Prog. Ser. 479, 13–24. https://doi.org/10.3354/meps10210.

Tamelander, T., Reigstad, M., Hop, H., Carroll, M.L., Wassmann, P., 2008. Pelagic and sympagic contribution of organic matter to zooplankton and vertical export in the Barents Sea marginal ice zone. Deep. Res. Part II Top. Stud. Oceanogr. 55, 2330–2339. https://doi.org/10.1016/j.dsr2.2008.05.019.

Trevizani, T.H., Figueira, R.C.L., Ribeiro, A.P., Theophilo, C.Y.S., Majer, A.P., Petti, M.A.V., Corbisier, T.N., Montone, R.C., 2016. Bioaccumulation of heavy metals in marine organisms and sediments from admiralty bay, King George Island, Antarctica. Mar. Pollut. Bull. 106, 366–371. https://doi.org/10.1016/j.marpolbul.2016.02.056.

Vizzini, S., Signa, G., Mazzola, A., 2016. Guano-derived nutrient subsidies drive food web structure in coastal ponds. PLoS One 11. https://doi.org/10.1371/journal.pone.0151018 e0151018.

Wing, S.R., Leichter, J.J., Wing, L.C., Stokes, D., Genovese, S.J., Mcmullin, R.M., Shatove, O.,A., 2018. Contribution of sea ice microbial production to Antarctic benthic communities is driven by sea ice dynamics and composition of functional guilds. Global Change Biol. 24, 3642–3653. https://doi.org/10.1111/gcb.14291.